

## VIII. Appendix

An analysis of variance for the top sieve takes the following form (for terminology, see any standard text on the analysis of variance, for example [18]):

### Analysis of variance including all four knockers

[The value of  $F$  for significance at the 5-percent level is about 10 and at the 1-percent level about 30.]

Source of variation	Degrees of freedom	Sum of squares	Variance	$F$ value
Knockers	3	3.255	1.085	93.0
Machines	1	0.0625	0.0625	5.36
Chars	1	131.1	131.1	11,230
Interactions: Machines and chars	1	0.16	0.16	13.7
Machines and knockers	3	2.0625	.6875	58.8
Chars and knockers	3	0.0525	.0175	1.5
Triple interaction (error)	3	.035	.01167	-----
Total	15	136.73	-----	-----

Since it is noted that the absence of a knocker (condition knocker 4) is the greatest cause of the variation, the above analysis of variance is repeated omitting  $K_4$ :

### Analysis of variance omitting $K_4$ (no knocker)

[The value of  $F$  for significance at the 5-percent level is about 20 and at the 1-percent level about 100.]

Source of variation	Top sieve		Second sieve		Third sieve		Pan	
	Variance	$F$	Variance	$F$	Variance	$F$	Variance	$F$
Knockers	0.0258	1.49	0.01	3	0.2580	1.2	0.01	-----
Machines	.8533	49	.0208	6.2	.1633	5.3	.48	-----
Chars	98.06	5,600	6.02	1,800	6.45	209	.03	-----
Interactions:								
Machines and chars	0.120	6.8	0.0208	6.2	0.0533	1.8	.12	-----
Machines and knockers	.0308	1.8	.0133	4	.0108	2.8	.01	-----
Chars and knockers	.0583	1.5	.0133	4	.0358	1.2	0	-----
Triple interaction (error)	.0175	-----	.0033	-----	.0308	-----	0	-----

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# First Spectrum of Arsenic

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The spectrum emitted by neutral arsenic atoms was observed photographically in the infrared, visible, and ultraviolet, and new lines were discovered in each spectral region. Measured wavelengths and estimated relative intensities are given for 330 lines, ranging from 1407.34 to 11679.9 Å in wavelength and from 1 to 2000 in intensity. More than 74 percent of the total number and 97 percent of the total intensity of observed lines have been explained as combinations of 30 odd energy levels arising from  $4s^2 4p^3$  and  $4s^2 4p^2 np$  electron configurations and 58 even levels from  $4s 4p^4$ ,  $4s^2 4p^2 ns$ , and  $4s^2 4p^2 nd$ . The average difference between observed and computed wave numbers is 0.14  $\text{cm}^{-1}$ . Most of the observed levels have been assigned to doublet and quartet terms, and spectral series of the type  $4s^2 4p^3 - 4s^2 4p^2 ns$  have been identified. Calculations based on these series yield an absolute value of 79165  $\text{cm}^{-1}$  for the ground state  $4s^2 4p^3 {}^4S_{3/2}$  of neutral arsenic atoms, that is, an ionization potential of  $9.81 \pm 0.01$  electron volts.

## I. Introduction

In 1929 Meggers and deBruin [1]<sup>2</sup> published a paper on the arc spectrum of arsenic, based on measurements of 54 ultraviolet lines (1889.85 to 3119.60 Å) and 23 infrared lines (7410.07 to 10023.98 Å). At that time this spectrum had not been observed in the region of shorter waves, and the assumption that the Blochs [2] had observed As I lines in spark spectra in the extreme ultraviolet could not be verified. Although it was not possible then to determine absolute term values from spectral series, the ground state was recognized as  ${}^4S^o$ , and by comparison with analogous terms in the spectra of neighboring elements the absolute value of this ground state was tentatively estimated as 80693  $\text{cm}^{-1}$ , which corresponded to an ionization potential of about 10 ev. This was 13 percent lower than the value  $11.54 \pm 0.5$  ev derived in 1922 by Ruark,

et al. [3] from experiments on low-voltage arcs in arsenic vapor.

A paper on spectra of arsenic in the extreme ultraviolet, 2500 to 710 Å, by Queney [4] reported about 300 arsenic lines from electrodeless discharges but added nothing to the As I spectrum.

The shorter waves of this spectrum were first investigated by K. R. Rao [5], who burned metallic arsenic in an arc between carbon poles and photographed the spectrum with an evacuated spectrograph containing a 1 m-radius grating, giving a scale of 8.6 Å/mm. He measured 64 lines between 1995.45 and 1563.08 Å with estimated probable errors of  $\pm 0.03$  Å. Because no spectral series could be found, Rao adopted the absolute value  ${}^4S^o = 93500 \text{ cm}^{-1}$  from the ionization potential 11.54 ev reported by Ruark, et al. [3].

In 1932 further investigations of the arc spectrum of arsenic were reported by A. S. Rao [6], who measured 160 ultraviolet As I lines (1995.45 to 1319.48 Å) on a hollow-cathode spectrogram having a scale of

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<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

17 Å/mm. He quoted infrared data from Meggers and deBruin [1], ultraviolet data (3119.576 to 1563.08 Å) from K.R. Rao [5], and classified 200 lines with 66 levels. Earlier interpretations of the As I spectrum were revised and extended, and an estimate of the ionization potential as 10.5 eV was derived from two members of several assumed series terms. In the light of present data, many of Rao's designations of spectral terms appear to be incorrect, the reality of some of his levels is doubtful, and his value of the ionization potential for arsenic is certainly too large.

In 1933 Hicks [7] attempted to obtain an absolute value of the spectral terms of arsenic by "the application of the own-multiple law to the separations". Mysterious calculations led him to a value of  $87945 \text{ cm}^{-1}$  for the ionization limit, and he stated that "this is equivalent to 10.85 volts, and closer to the value  $11.52 \pm .5$  referred to by Rao than his 85000 with 10.5 volts". It now appears that this correction was wrong in both direction and magnitude.

The only other investigation of the first spectrum of arsenic published during the past 20 years deals with the Zeeman effect. Green and Barrows [8], in 1935, published Zeeman patterns for 11 lines (2288.2 to 3033.0 Å), derived  $g$ -values for 13 levels, and concluded that "the levels of As I are so close to  $LS$  coupling that the  $g$ -values are almost normal".

The lack of a reliable ionization potential was inspiration and justification for another investigation of the first spectrum of arsenic. Such an investigation has been made at the National Bureau of Standards from time to time during the past 20 years, and as a result, the As I spectrum has been exhaustively explored photographically from 12500 Å in the infrared to 1200 Å in the ultraviolet. This spectrum has been found to consist of three separated groups of lines, 71 infrared, 46 visible, and 210 ultraviolet. More than 74 percent of the total number and 97 percent of the total intensity of observed As I lines have been explained as combinations of 88 atomic-energy levels, and a principal ionization potential of 9.81 eV has been calculated with confidence. Because further investigation of this spectrum is neither likely nor profitable, this final report is now presented.

## II. Wavelength Measurements

The infrared As I lines reported by Meggers and deBruin [1] were observed with photographic plates sensitized in the laboratory by bathing them in dilute solutions of neocyanine, and the greatest wavelength that could be recorded was 10024 Å. In 1934 "Xenocyanine Plates" prepared by the Eastman Kodak Co. permitted an extension of the infrared recording of As I lines to 10888 Å, and in 1940 Eastman I-Z plates were used to explore this spectrum to 12500 Å. No As I lines were recorded beyond 11680 Å, but this wavelength is more than 1000 Å greater than the limit observed radiometrically by Randall [9] in 1911.

The light sources, spectrographs, and standard

wavelengths employed in observing the infrared, visible, and air-transparent ultraviolet As I spectrum were described in detail by Meggers and deBruin [1].

A number of visible lines not previously noted in the arc spectrum of arsenic and not identifiable with impurities were observed in 1929 [1], but few details were given because no structural connection was found between the visible lines and the invisible ones. Such a connection was first found in 1932 by deBruin,<sup>3</sup> who saw that some of the visible lines exhibited the same wave-number differences as some infrared ones. At that time it was not possible to classify and interpret all the visible lines, but this was facilitated by the more recent extensions of the infrared data.

The most important improvements of As I data were made in the extreme ultraviolet, from arc spectrograms exposed at Princeton University and measured at the National Bureau of Standards. The spectrograms were made with a normal incidence vacuum spectrograph having a 2 m-radius glass grating ruled 30,000 lines per inch. The dispersion is 4.2 Å/mm and the definition and resolving power are excellent, but Rowland ghosts are prominent on strong exposures. All the identified ghosts contributed to determinations of the wavelengths of their respective parent lines.

Our first attempt to observe the short waves of the As I spectrum was made in 1940 with electrodes of 25 percent As and 75 percent Cu prepared in the Metallurgy Division of this Bureau. Four spectrograms were measured relative to copper standards, but only 100 As I lines were found between 1995.43 and 1472.38 Å. Because the arsenic spectrum could not be fully developed with this alloy without greatly overexposing the copper spectra, additional spectrograms were made in 1949 with metallic arsenic in a cupped carbon electrode opposite a copper electrode. These were highly satisfactory for the final description of the As I spectrum to its ultraviolet limit near 1400 Å; after eliminating lines due to As II, impurities, and ghosts, they yielded 168 As I lines between 1995.43 and 1407.34 Å. These wavelengths were measured relative to Cu I and Cu II lines given in Shenstone's papers [10] supplemented by carbon, nitrogen, and oxygen "impurity" lines recommended as tentative standards by Boyce and Robinson [11]. All except the weak lines were measured on six or seven spectrograms, and the agreement between determinations, as well as the agreement between values observed and calculated from atomic-energy levels, prove that the probable error rarely exceeds  $\pm 0.01$  Å. The complete list of observed lines was compared with the Table of Principal Lines of all Elements [12] for the purpose of identifying possible impurities, and the ultraviolet portion was also compared with a description by Rao [13] of the first spark spectrum of arsenic for the purpose of eliminating about 10 As II lines that appeared in the arc spectrum.

Measured wavelengths and estimated intensities of 330 lines characteristic of neutral arsenic atoms are

<sup>3</sup> Communicated by T. L. deBruin to W. F. Meggers in a note dated Feb. 27, 1932.

presented in the first and second columns, respectively, of table 1. The wavelengths greater than 2000 Å are valid for standard air; those smaller than 2000 Å are vacuum values. The intensity numbers are assigned from visual comparisons of the blackness and width of slit images on the most strongly exposed spectrograms; they are comparable only for

lines in limited regions of spectra and obviously decline rapidly beyond 11000 Å as photographic sensitivity decreases for increasing wavelength. In addition to intensity, the character of certain lines is indicated by symbols:  $R$ =wide self-reversal,  $r$ =narrow self-reversal,  $h$ =hazy,  $e$ =observed at electrode.

TABLE 1. First spectrum of arsenic (As I)

$\lambda_{\text{air}}$ Å	Intensity, character	Wave No. vac. cm <sup>-1</sup>	Obs.— Calc. Wave No. 0.1 cm <sup>-1</sup>	Term combination	$\lambda_{\text{air}}$ Å	Intensity, character	Wave No. vac. cm <sup>-1</sup>	Obs.— Calc. Wave No. 0.1 cm <sup>-1</sup>	Term combination
1	2	3	4	5	1	2	3	4	5
11679.9	3	8559.37			7863.43	4	12713.61	0	$5s^4P_{1/2}-5p^2P_{0/2}$
11520.9	10	8677.54	0	$5s^2P_{1/2}-5p^4P_{3/2}$	7829.82	2	12768.17	+1	$5p^4D_{3/2}-4d^2D_{2/2}$
11377.1	4	8787.19	+1	$5s^4P_{2/2}-5p^4D_{3/2}$	7648.15	2	13071.46		
11244.5	10	8890.79	+1	$5s^2P_{0/2}-5p^4P_{0/2}$	7410.02	8	13491.53	+1	$5p^4D_{3/2}-75176$
10888.82	20	9181.22	-1	$5s^4P_{1/2}-5p^4D_{0/2}$	7384.97	10	13537.29		
10808.11	50	9249.78	0	$5s^4P_{1/2}-5p^4D_{1/2}$	7384.62	10	13537.94		
10793.37	8	9262.42	0	$5s^2P_{0/2}-5p^4P_{1/2}$	6338.94	40	15771.16	-1	$5s^2P_{1/2}-5p^2D_{3/2}$
10780.36	5	9273.59	0	$5s^2D_{1/2}-5p^2D_{1/2}$	6176.68	1	16185.46		
10614.07	200	9418.87	+1	$5s^2P_{0/2}-5p^2D_{1/2}$	6049.48	5h	16525.78	+1	$5s^2P_{1/2}-6p^4D_{3/2}$
10575.02	100	9453.65	0	$5s^2P_{1/2}-5p^2S_{0/2}$	5815.40	2h	17190.97	+1	$5s^2P_{1/2}-5p^2P_{0/2}$
10490.29	2h	9530.02			5751.85	5h	17380.90	-1	$5s^2P_{0/2}-6p^4D_{1/2}$
10477.30	4	9541.83	0	$5s^2D_{1/2}-5p^2D_{2/2}$	5739.54	2h	17418.18		
10455.64	20	9561.60	0	$5s^2D_{2/2}-5p^2D_{2/2}$	5534.47	3	18063.57	+1	$5s^2P_{0/2}-6p^2S_{0/2}$
10453.09	100	9563.93	0	$5s^2P_{1/2}-5p^2D_{2/2}$	5497.10	4	18186.37		
					5494.40	5	18195.31	0	$5s^2P_{1/2}-6p^2P_{0/2}$
10445.6	3h	9570.84	+2	$5p^2D_{1/2}-4d^2P_{1/2}$	5451.32	150	18339.10	0	$5s^2P_{1/2}-6p^2D_{2/2}$
10325.74	10	9681.88	+1	$5s^2D_{1/2}-6p^4D_{1/2}$	5422.66	2	18436.02		
10304.82	5	9701.54	-1	$5s^2D_{2/2}-6p^4D_{1/2}$	5408.13	100	18485.56	-2	$5s^2P_{0/2}-6p^2D_{1/2}$
10286.85	50	9718.49	0	$5s^2P_{1/2}-5p^2P_{0/2}$	5363.54	60	18639.23	-3	$5s^2P_{1/2}-6p^2P_{1/2}$
10024.04	400	9973.30	0	$5s^4P_{2/2}-5p^4D_{3/2}$	5361.12	10	18647.65		
10010.63	100	9986.65	0	$5s^2D_{1/2}-5p^2F_{2/2}$	5357.42	1h	18660.53	-1	$5s^2P_{0/2}-5p^2P_{0/2}$
9990.87	5	10006.40	0	$5s^2D_{2/2}-5p^2F_{2/2}$	5318.76	5	18796.16	+1	$5s^2P_{0/2}-5p^2P_{1/2}$
9923.05	400	10074.78	0	$5s^4P_{1/2}-5p^4D_{1/2}$	5212.14	5	19180.65		
9915.71	200	10082.24	-1	$5s^2P_{1/2}-5p^2P_{1/2}$	5210.23	20	19187.68	0	$5s^4P_{0/2}-6p^4P_{0/2}$
9900.55	150	10097.68	0	$5s^4P_{0/2}-5p^4D_{0/2}$	5203.84	4	19211.24	0	$5s^4P_{1/2}-5p^2F_{2/2}$
9886.05	100	10112.49	0	$5s^2D_{2/2}-5p^2F_{2/2}$	5196.20	50	19239.49	0	$5s^4P_{1/2}-6p^4P_{1/2}$
9869.5	2	10129.5			5141.63	100	19443.68	0	$5s^4P_{2/2}-6p^4D_{3/2}$
9850.4	1	10149.1			5130.78	80	19484.80	+1	$5s^2P_{0/2}-6p^4S_{1/2}$
9833.76	300	10166.26	+1	$5s^4P_{0/2}-5p^4D_{1/2}$	5121.34	100	19520.72	-1	$5s^4P_{1/2}-6p^4D_{2/2}$
9781.32	30	10220.77			5105.55	30 Cu?	19581.09	0	$5s^4P_{0/2}-6p^4D_{0/2}$
					5103.53	20	19588.84	-1	$5s^4P_{1/2}-6p^2S_{0/2}$
9772.08	7	10230.43			5099.59	60	19603.97	0	$5s^4P_{2/2}-6p^4P_{2/2}$
9721.8	1	10283.3			5083.76	10	19665.02	0	$5s^2P_{0/2}-6p^2P_{0/2}$
9714.64	10	10290.92			5068.98	100	19722.35	0	$5s^4P_{2/2}-6p^4S_{1/2}$
9690.83	10	10316.20	+2	$5s^2D_{2/2}-6p^4D_{2/2}$	5043.31	50	19822.74	-1	$5s^4P_{0/2}-6p^4D_{1/2}$
9654.54	10	10354.98			4995.83	8	20011.13	-1	$5s^4P_{1/2}-6p^2D_{1/2}$
9648.06	20	10361.94			4987.02	6h	20046.48	0	$5s^4P_{2/2}-6p^2D_{2/2}$
9645.8	3	10364.4	+1	$5s^2D_{1/2}-6p^2S_{0/2}$	4952.56	10	20185.96	0	$5s^4P_{1/2}-5p^2P_{0/2}$
9626.70	400	10384.93	0	$5s^4P_{2/2}-5p^4P_{2/2}$	4919.49	2	20321.65	+1	$5s^4P_{1/2}-5p^2P_{1/2}$
9597.95	300	10416.04	-1	$5s^4P_{1/2}-5p^4P_{0/2}$	4910.23	10h	20359.98		
9510.9	3	10511.4	0	$5s^2P_{0/2}-5p^4S_{1/2}$	4873.78	2h	20512.24		
9300.61	250	10749.04	-1	$5s^4P_{2/2}-5p^4S_{1/2}$	4785.27	3h	20891.64	-1	$5s^4P_{1/2}-6p^4P_{2/2}$
9267.28	150	10787.70	-1	$5s^4P_{1/2}-5p^4P_{1/2}$	4777.02	1h	20927.72	+1	$5s^4P_{0/2}-6p^2D_{1/2}$
9165.6	3 Cu?	10907.4	+11	$(5s^2D_{1/2}-6p^2D_{1/2})$	4758.28	5h	21010.14	0	$5s^4P_{1/2}-6p^4S_{1/2}$
9134.78	50	10944.17	0	$5s^4P_{1/2}-5p^2D_{1/2}$	4622.82	6h	21625.78		
9120.32	10	10961.52	+1	$5s^2D_{1/2}-5p^2P_{0/2}$	4621.27	4h	21633.03		
9027.8	2	11073.9			4355.39	10h	22953.63		
9008.95	2	11097.02	+1	$5s^2D_{1/2}-5p^2P_{1/2}$	4342.05	10h	23024.15		
8993.05	20	11116.65	-1	$5s^2D_{2/2}-5p^2P_{1/2}$	4336.15	5h	23055.47		
8980.13	5	11132.64	-3	$5p^4D_{0/2}-4d^2P_{0/2}$	4320.12	3h	23141.02		
8935.56	50	11188.17	0	$5s^2P_{0/2}-5p^2P_{0/2}$	4313.16	4h	23178.36		
8874.8	2h	11264.8	-2	$5p^4D_{1/2}-4d^2P_{1/2}$	4301.56	5h	23240.87		
8869.66	100	11271.30	0	$5s^4P_{2/2}-5p^2D_{2/2}$	3119.60	50	32046.1	-2	$4p^3^2P_{1/2}-5s^4P_{0/2}$
8821.73	150	11332.41	-1	$5s^4P_{0/2}-5p^4P_{0/2}$	3075.32	20	32507.5	-2	$4p^3^2P_{0/2}-5s^4P_{0/2}$
8654.14	100	11551.99	0	$5s^2P_{0/2}-5p^2P_{1/2}$	3032.85	40	32962.7	0	$4p^3^2P_{1/2}-5s^4P_{1/2}$
8646.03	3	11562.83			2990.99	20	33424.0	-1	$4p^3^2P_{0/2}-5s^4P_{1/2}$
8564.71	100	11672.62	0	$5s^4P_{1/2}-5p^4P_{2/2}$	2918.82	2	34250.4	0	$4p^3^2P_{1/2}-5s^4P_{2/2}$
8541.60	50	11704.20	0	$5s^4P_{0/2}-5p^4P_{1/2}$	2898.71	50r	34488.0	-1	$4p^3^2P_{1/2}-5s^4P_{0/2}$
8455.1	8	11823.9			2860.44	100r	34949.4	-1	$4p^3^2P_{0/2}-5s^4P_{0/2}$
8428.91	100	11860.66	+1	$5s^4P_{0/2}-5p^2D_{1/2}$	2780.22	200r	35957.8	0	$4p^3^2P_{1/2}-5s^4P_{1/2}$
8354.84	10	11965.82	0	$5s^2D_{1/2}-6p^2P_{0/2}$	2745.00	50r	36419.1	-1	$4p^3^2P_{0/2}-5s^4P_{1/2}$
8305.61	50	12036.75	0	$5s^4P_{1/2}-5p^4S_{1/2}$	2492.91	50	40101.7	+4	$4p^3^2D_{1/2}-5s^4P_{0/2}$
8242.15	20	12129.43	0	$5s^2D_{2/2}-6p^2D_{2/2}$	2456.53	200r	40695.5	-1	$4p^3^2D_{3/2}-5s^4P_{1/2}$
8055.72	5h	12410.13	+1	$5s^2D_{1/2}-6p^2P_{1/2}$	2437.23	50	41017.7	0	$4p^3^2D_{1/2}-5s^4P_{1/2}$
8042.95	8	12429.83	0	$5s^2D_{2/2}-6p^2P_{1/2}$	2381.18	150r	41983.2	-1	$4p^3^2D_{3/2}-5s^4P_{2/2}$
7960.27	30	12558.94	-1	$5s^4P_{1/2}-5p^2D_{2/2}$	2370.77	100r	42167.5	0	$4p^3^2P_{1/2}-5s^4D_{2/2}$



TABLE 1. First spectrum of arsenic (As I)—Continued

$\lambda_{\text{air}}$ Å	Intensity, character	Wave No. vac. cm <sup>-1</sup>	Obs.— Calc. Wave No. 1.0 cm <sup>-1</sup>	Term combination	$\lambda_{\text{vac.}}$ Å	Intensity, character	Wave No. vac. cm <sup>-1</sup>	Obs.— Calc. Wave No. 0.1 cm <sup>-1</sup>	Term combination
1	2	3	4	5	1	2	3	4	5
2369.67	80r	42187.1	-2	$4p^3 \ ^2P_{1/2}^o - 5s' \ ^2D_{3/2}$	1844.57	40	54213.2	-1	$4p^3 \ ^2P_{3/2}^o - 5s' \ ^2S_{1/2}$
2363.05	10	42305.2	-2	$4p^3 \ ^2D_{1/2}^o - 5s' \ ^4P_{3/2}$	1844.36	40	54219.3	+3	$4p^3 \ ^2D_{1/2}^o - 4p^4 \ ^2P_{1/2}$
2349.84	500R	42543.0	-1	$4p^3 \ ^2D_{1/2}^o - 5s' \ ^2P_{3/2}$	1840.48	10	54333.6	+3	$4p^3 \ ^2P_{3/2}^o - 72519$
2344.03	50	42648.5	-2	$4p^3 \ ^2P_{3/2}^o - 5s' \ ^2D_{3/2}$	1831.74	30	54592.9	0	$4p^3 \ ^2P_{3/2}^o - 72779$
2288.12	500R	43690.5	-2	$4p^3 \ ^2D_{3/2}^o - 5s' \ ^2P_{1/2}$	1831.30	50	54606.0	+7	$4p^3 \ ^4S_{1/2} - 5s' \ ^2P_{1/2}$
2271.36	50	44012.8	0	$4p^3 \ ^2D_{1/2}^o - 5s' \ ^2P_{3/2}$	1821.32	2	54905.2	+3	$4p^3 \ ^2D_{1/2}^o - 4p^4 \ ^2P_{3/2}$
2266.70	25	44103.3	-3	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^4P_{3/2}$	1818.59	5h	54987.7	+2	$4p^3 \ ^2P_{1/2}^o - 73635$
2228.66	20	44856.0	-1	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^4P_{1/2}$	1816.72	10	55044.3		
2205.97	15	45317.4	-1	$4p^3 \ ^2P_{3/2}^o - 4d' \ ^4P_{3/2}$	1806.15	200	55366.4	0	$4p^3 \ ^4S_{1/2} - 4p^4 \ ^4P_{3/2}$
2205.16	10	45334.0	-2	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^4P_{3/2}$					
2198.34	5	45474.6	+1	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2P_{3/2}$	1803.46	10h	55449.0	+1	$4p^3 \ ^2P_{3/2}^o - 73635$
2187.75	5	45694.7	-2	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2D_{3/2}$	1801.92	3	55496.4	+1	$4p^3 \ ^2P_{1/2}^o - 74143$
2182.94	20	45795.5	-1	$4p^3 \ ^2P_{3/2}^o - 4d' \ ^4P_{3/2}$	1799.51	2	55570.7	+1	$4p^3 \ ^2D_{3/2}^o - 4d' \ ^2P_{1/2}$
2176.26	5	45935.9	0	$4p^3 \ ^2P_{3/2}^o - 4d' \ ^2P_{3/2}$	1798.61	9	55598.5		
2165.52	150	46163.8	-2	$4p^3 \ ^2P_{1/2}^o - 4p^4 \ ^2P_{1/2}$	1791.77	40	55810.7	-1	$4p^3 \ ^2D_{3/2}^o - 4d' \ ^2D_{3/2}$
2144.08	100	46625.3	-1	$4p^3 \ ^2P_{3/2}^o - 4p^4 \ ^2P_{1/2}$	1789.85	50	55870.6	0	$4p^3 \ ^2D_{3/2}^o - 4d' \ ^2F_{3/2}$
2142.80	2	46653.2			1789.14	15	55892.8	+1	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^2P_{1/2}$
2133.80	50	46849.9	0	$4p^3 \ ^2P_{1/2}^o - 4p^4 \ ^2P_{3/2}$	1787.07	3	55957.5	-2	$4p^3 \ ^2P_{3/2}^o - 74143$
2112.99	100	47311.3	0	$4p^3 \ ^2P_{3/2}^o - 4p^4 \ ^2P_{3/2}$	1785.84	3	55996.1	+3	$4p^3 \ ^2P_{1/2}^o - 75086$
2089.74	6	47837.6	-1	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2P_{1/2}$	1781.48	50	56133.1	+2	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^2D_{3/2}$
2085.25	30	47940.6	-2	$4p^3 \ ^2P_{1/2}^o - 4p^4 \ ^2S_{1/2}$	1780.52	50	56163.4	+4	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2D_{1/2}$
2079.30	7	48077.7	-2	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2D_{3/2}$	1775.12	2	56334.2		
2069.78	30	48298.8	-3	$4p^3 \ ^2P_{3/2}^o - 4d' \ ^2P_{3/2}$	1772.54	8	56416.2	0	$4p^3 \ ^2D_{1/2}^o - 6s' \ ^4P_{3/2}$
2067.11	20	48361.2	0	$4p^3 \ ^2P_{1/2}^o - 6s' \ ^4P_{3/2}$	1771.84	2	56438.5	0	$4p^3 \ ^2P_{1/2}^o - 75086$
2065.36	50	48402.2	0	$4p^3 \ ^2P_{3/2}^o - 4p^4 \ ^2S_{1/2}$	1768.97	5	56530.1	+12	$4p^3 \ ^2P_{1/2}^o - 75176?$
2061.61	3	48490.2			1767.97	6e, h?	56562.0		
2047.57	50	48822.6	0	$4p^3 \ ^2P_{3/2}^o - 6s' \ ^4P_{3/2}$	1758.60	100	56863.6	0	$4p^3 \ ^4S_{1/2} - 4p^4 \ ^4P_{1/2}$
2028.86	2	49272.8	+1	$4p^3 \ ^2P_{1/2}^o - 6s' \ ^4P_{1/2}$	1757.47	4	56900.0	+1	$4p^3 \ ^2P_{3/2}^o - 75086$
2024.34	5	49382.8			1756.51	2h	56931.1	-1	$4p^3 \ ^2P_{1/2}^o - 75578$
2013.32	100	49653.1	0	$4p^3 \ ^2P_{1/2}^o - 4p^4 \ ^2D_{1/2}$	1754.21	10	57005.7	+1	$4p^3 \ ^2D_{3/2}^o - 6s' \ ^4P_{1/2}$
2012.76	15	49666.9	-1	$4p^3 \ ^2P_{1/2}^o - 6s' \ ^2P_{3/2}$	1750.37	2	57130.8		
2010.04	20	49734.0	-1	$4p^3 \ ^2P_{3/2}^o - 6s' \ ^4P_{1/2}$	1749.72	1e, h	57152.0	+1	$4p^3 \ ^2P_{1/2}^o - 75799$
2009.19	100r	49755.1	-1	$4p^3 \ ^2P_{1/2}^o - 4p^4 \ ^2D_{3/2}$	1745.60	1	57286.9		
2003.34	300r	49900.4	0	$4p^3 \ ^2D_{3/2}^o - 5s' \ ^2D_{3/2}$	1742.59	10	57385.8	-2	$4p^3 \ ^2D_{3/2}^o - 4p^4 \ ^2D_{1/2}$
2002.54	20	49920.3	+1	$4p^3 \ ^2D_{3/2}^o - 5s' \ ^2D_{1/2}$	1741.28	10	57429.0	+3	$4p^3 \ ^2P_{1/2}^o - 76076$
vac.					1740.93	3	57440.6		
1995.43	100r	50114.5	0	$4p^3 \ ^2P_{3/2}^o - 4p^4 \ ^2D_{1/2}$	1739.49	60	57488.1	0	$4p^3 \ ^2D_{3/2}^o - 4p^4 \ ^2D_{3/2}$
1994.89	20	50128.3	-1	$4p^3 \ ^2P_{3/2}^o - 6s' \ ^2P_{3/2}$	1735.70	3	57613.6	+3	$4p^3 \ ^4S_{1/2} - 4p^4 \ ^4P_{3/2}$
1991.13	100r	50222.7	+2	$4p^3 \ ^2D_{1/2}^o - 5s' \ ^2D_{3/2}$	1732.44	30	57708.1	0	$4p^3 \ ^2P_{3/2}^o - 75799$
1990.35	200r	50242.4	+1	$4p^3 \ ^2D_{1/2}^o - 5s' \ ^2D_{1/2}$	1732.44	30	57708.1	0	$4p^3 \ ^2P_{1/2}^o - 4p^4 \ ^2D_{1/2}$
1973.65	3	50667.5	+2	$4p^3 \ ^2P_{1/2}^o - 6s' \ ^4P_{3/2}$	1732.44	30	57722.1	+1	$4p^3 \ ^2D_{1/2}^o - 6s' \ ^2P_{3/2}$
1972.62	1000R	50694.0	+2	$4p^3 \ ^4S_{1/2} - 5s' \ ^4P_{3/2}$	1729.80	30	57810.2	0	$4p^3 \ ^2D_{1/2}^o - 4p^4 \ ^2D_{3/2}$
1960.89	2	50997.2	-1	$4p^3 \ ^2P_{1/2}^o - 69644$	1727.38	4	57891.1	+10	$4p^3 \ ^2P_{3/2}^o - 76076?$
1958.91	40r	51048.8	+1	$4p^3 \ ^2P_{1/2}^o - 6s' \ ^2P_{1/2}$	1724.77	7	57978.7		
1958.82	20	51051.1	+3	$4p^3 \ ^2P_{1/2}^o - 69698$	1722.37	4e	58059.5		
1950.38	2	51272.1			1718.55	1	58188.6	+5	$4p^3 \ ^2P_{1/2}^o - 76835$
1943.30	2e	51458.9	+2	$4p^3 \ ^2P_{3/2}^o - 69644$	1712.32	10	58400.3	+1	$4p^3 \ ^2D_{3/2}^o - 6s' \ ^4P_{3/2}$
1941.36	5	51510.3	+2	$4p^3 \ ^2P_{3/2}^o - 6s' \ ^2P_{1/2}$	1710.16	7h	58474.1	-1	$4p^3 \ ^2P_{1/2}^o - 77121$
1937.59	1500R	51610.4	+2	$4p^3 \ ^4S_{1/2} - 5s' \ ^4P_{1/2}$	1709.26	2h	58504.8		
1929.14	3	51836.6	+1	$4p^3 \ ^2D_{3/2}^o - 4d' \ ^4P_{3/2}$	1709.03	2	58512.7		
1928.30	1	51859.2			1705.74	4	58625.6	+6	$4p^3 \ ^2P_{1/2}^o - 77272$
1919.72	1	52090.9			1702.94	3	58722.0	-3	$4p^3 \ ^2D_{1/2}^o - 6s' \ ^4P_{3/2}$
1918.39	3	52127.0			1701.22	30	58781.3	-3	$4p^3 \ ^2D_{3/2}^o - 6s' \ ^2P_{1/2}$
1917.21	20	52159.1	+5	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^4P_{3/2}$	1701.16	15	58783.4	-3	$4p^3 \ ^2D_{3/2}^o - 69698$
1908.13	1	52407.3	-4	$4p^3 \ ^2P_{1/2}^o - 71055$	1691.87	7	59106.2	+4	$4p^3 \ ^2D_{1/2}^o - 69698$
1902.31	6	52567.7			1687.12	3e	59272.6		
1901.54	5	52589.0	0	$4p^3 \ ^2D_{3/2}^o - 4d' \ ^4P_{1/2}$	1684.63	2e	59360.2		
1891.47	5	52868.9	-2	$4p^3 \ ^2P_{3/2}^o - 71055$	1681.47	1	59471.8		
1890.42	2000R	52898.2	+3	$4p^3 \ ^4S_{1/2} - 5s' \ ^4P_{3/2}$	1679.14	2	59554.3		
1889.95	5	52911.4	+3	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^4P_{3/2}$	1674.59	3	59716.1		
1881.96	40	53136.1	+5	$4p^3 \ ^4S_{1/2} - 5s' \ ^2P_{3/2}$	1671.88	2	59812.9		
1876.98	2	53277.1	+2	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2P_{3/2}$	1670.79	4	59851.9		
1873.02	40	53389.6	+4	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^4P_{3/2}$	1670.12	2	59875.9		
1871.68	30	53427.9	+1	$4p^3 \ ^2D_{3/2}^o - 4d' \ ^2D_{1/2}$	1662.76	2	60141.0	+4	$4p^3 \ ^2D_{3/2}^o - 71055$
1871.14	2	53443.4			1653.92	4	60462.4	-3	$4p^3 \ ^2D_{1/2}^o - 71055$
1869.94	15	53477.6	+1	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2P_{1/2}$	1649.55	2	60622.6		
1865.10	8	53616.6			1644.33	5	60815.0	0	$4p^3 \ ^4S_{1/2} - 5s' \ ^2D_{3/2}$
1860.87	5	53738.3	0	$4p^3 \ ^2P_{3/2}^o - 4d' \ ^2P_{3/2}$	1643.79	2	60835.0	+2	$4p^3 \ ^4S_{1/2} - 5s' \ ^2D_{1/2}$
1860.46	80	53750.1	+2	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^2D_{1/2}$	1633.71	5	61210.4	0	$4p^3 \ ^2D_{3/2}^o - 4d' \ ^2P_{1/2}$
1860.40	80	53751.9	0	$4p^3 \ ^2P_{1/2}^o - 5s' \ ^2S_{1/2}$	1630.48	4	61331.6	-3	$4p^3 \ ^2P_{1/2}^o - 4d' \ ^2P_{3/2}$
1856.24	2	53872.3	+4	$4p^3 \ ^2P_{1/2}^o - 72519$	1625.17	1	61532.0	-5	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^2P_{1/2}$
1855.39	10	53897.0	+1	$4p^3 \ ^2D_{3/2}^o - 4p^4 \ ^2P_{1/2}$	1623.26	2	61604.4	-4	$4p^3 \ ^2D_{3/2}^o - 72519$
1853.95	3	53938.9	0	$4p^3 \ ^2P_{3/2}^o - 4d' \ ^2P_{3/2}$	1620.94	5	61692.6		
1853.21	20	53960.4			1616.44	6	61864.5	+1	$4p^3 \ ^2D_{3/2}^o - 72779$
1850.24	40	54047.0	10	$4p^3 \ ^2D_{1/2}^o - 4d' \ ^2P_{3/2}$	1614.82	5	61926.5	-4	$4p^3 \ ^2D_{1/2}^o - 72519$
1847.32	10	54132.5	+0	$4p^3 \ ^2P_{1/2}^o - 72779$	1612.57	4	62012.8		



TABLE 1. First spectrum of arsenic (As I)—Continued

$\lambda$ vac Å	Intensity, character	Wave No. vac. cm <sup>-1</sup>	Obs.— Calc. Wave No. 0.1 cm <sup>-1</sup>	Term combination	$\lambda$ vac Å	Intensity, character	Wave No. vac. cm <sup>-1</sup>	Obs.— Calc. Wave No. 0.1 cm <sup>-1</sup>	Term combination
1	2	3	4	5	1	2	3	4	5
1608.07	3	62186.3	—2	$4p^3\ ^2D_{3/2}-72779$	1516.97	1e	65920.9	—1	$4p^3\ ^2D_{3/2}-76835$
1597.48	2	62598.6			1515.48	20h	65985.7		
1596.13	2	62651.5	+1	$4p^3\ ^2D_{3/2}-73566$	1510.70	6h	66194.5		
1594.39	1e	62719.9	—5	$4p^3\ ^2D_{3/2}-73635$	1510.41	6h	66207.2	+1	$4p^3\ ^2D_{3/2}-77121$
1593.60	100R	62751.0	—1	$4p^3\ ^4S_{3/2}-4d\ ^4P_{3/2}$	1509.70	3	66238.3		
1587.97	20	62973.5	0	$4p^3\ ^2D_{3/2}-73566$	1509.60	3	66242.7	—4	$4p^3\ ^2D_{3/2}-76835$
1583.90	2	63135.3	+2	$4p^3\ ^2D_{3/2}-74049$	1506.99	2	66357.4	—5	$4p^3\ ^2D_{3/2}-77272$
1575.87	20	63457.0	—2	$4p^3\ ^2D_{3/2}-74049$	1504.09	2	66485.4	+2	$4p^3\ ^4S_{3/2}-4d\ ^2P_{1/2}$
1574.72	30r	63503.4	—2	$4p^3\ ^4S_{3/2}-4d\ ^4P_{1/2}$	1503.47	1e,h	66512.8		
1573.85	60	63538.5	0	$4p^3\ ^2D_{3/2}-4d\ ^2D_{3/2}$	1492.81	1e	66987.8		
1572.19	1e,h	63605.5			1492.34	4	67008.9	+2	$4p^3\ ^4S_{3/2}-6s\ ^4P_{3/2}$
1566.39	15	63841.1			1484.36	5h	67369.1		
1565.05	7	63895.7	—2	$4p^3\ ^2D_{3/2}-4d\ ^2D_{3/2}$	1472.32	4	67920.0	—2	$4p^3\ ^4S_{3/2}-6s\ ^4P_{1/2}$
1562.95	10	63981.6	—1	$4p^3\ ^4S_{3/2}-4d\ ^4P_{1/2}$	1470.09	3e	68023.0		
1559.53	4	64121.9	—1	$4p^3\ ^4S_{3/2}-4d\ ^2P_{3/2}$	1468.42	2e	68100.4		
1559.48	4	64124.1			1464.10	2e	68301.1	+5	$4p^3\ ^4S_{3/2}-4p^4\ ^2D_{3/2}$
1558.28	4d+Cu?	64173.3			1461.92	3e,g?	68403.0	+3	$4p^3\ ^4S_{3/2}-4p^4\ ^2D_{3/2}$
1557.20	30	64217.8	—2	$4p^3\ ^2D_{3/2}-4d\ ^2D_{3/2}$	1442.69	5	69315.0	+2	$4p^3\ ^4S_{3/2}-6s\ ^4P_{21/2}$
1556.14	40	64261.6	—2	$4p^3\ ^2D_{3/2}-75176$	1434.77	3e	69697.6	—7	$4p^3\ ^4S_{3/2}-69698$
1554.19	4	64342.2	—2	$4p^3\ ^4S_{3/2}-4d\ ^2D_{3/2}$	1434.66	1e,h	69702.9		
1547.59	3	64616.6			1422.95	2e,h	70276.5		
1546.45	2	64664.2	+1	$4p^3\ ^2D_{3/2}-75578$	1412.95	2e,h	70773.9		
1542.94	4	64811.3	—2	$4p^3\ ^4S_{3/2}-4p^4\ ^2P_{1/2}$	1407.34	2e	71056.0		
1538.79	20	64986.1	—1	$4p^3\ ^2D_{3/2}-75578$					
1534.65	4	65161.4	—2	$4p^3\ ^2D_{3/2}-76076$					
1533.67	3	65203.1							
1533.60	3	65206.0	—9	$4p^3\ ^2D_{3/2}-75799?$					
1526.78	2	65497.3	—1	$4p^3\ ^4S_{3/2}-4p^4\ ^2P_{3/2}$					
1521.81	1e	65711.2							
1518.10	1e	65871.8							

### III. Analysis of the First Spectrum of Arsenic

The above-described efforts to obtain a better description of the As I spectrum were made primarily for the purpose of establishing atomic energy levels characteristic of neutral arsenic atoms and to determine the spectroscopic ionization potential.

#### 1. Observed As I Lines

The first two columns of table 1 contain the observational material upon which a new analysis is based, but as atomic energy levels are directly proportional to frequencies or wave numbers, the wavelengths in column 1 were converted to vacuum wave numbers in column 3. Wave lengths shorter than 2000 Å, being vacuum values, were converted to vacuum wave numbers by calculating the reciprocals [14] of the observed wavelengths. Vacuum wave numbers for lines between 2000 and 10000 Å were taken directly from Kayser's Table of Wave Numbers [15], but for lines of greater wavelength the values were obtained by computing the reciprocals of the wavelengths after correcting them to vacuum with the aid of the atmospheric dispersion formula of Meggers and Peters [16].

The first regularities among arsenic lines were discovered in 1894 by Kayser and Runge [17], who found 20 ultraviolet lines to be connected by wave-number differences of 461 and 8058. Thirty years later, another significant wave-number difference was found by Ruark, et al. [3], and in 1927 McLennan

and McLay [18] interpreted these constant differences as intervals between five low-energy odd levels, namely  $^4S_{3/2}$ ,  $^2D_{3/2}$ ,  $^2D_{5/2}$ ,  $^2P_{3/2}$ ,  $^2P_{1/2}$ , arising from the electron configuration  $4s^2 4p^3$ . Naturally, the separations of these five levels were exploited in each subsequent attempt to extend the analysis of the As I spectrum; they have accounted for most of the observed ultraviolet lines and coincidentally disclosed a considerable number of high-energy even levels, the lowest of which are important for the classification of visible and infrared lines, thus revealing other high-energy odd levels. In the present instance, the separations of the five lowest odd levels ( $0.0, 10592.5, 10914.6, 18186.1, 18647.5$  cm<sup>-1</sup>), when applied to the wave numbers of ultraviolet As I lines, yielded about 50 even levels ( $50693.8$  to  $77272.5$  cm<sup>-1</sup>), and the separations of seven lowest even levels ( $50693.8, 51610.2, 52897.9, 53135.6, 54605.3, 60815.0, 60834.8$  cm<sup>-1</sup>), when applied to the wave numbers of visible and infrared lines, led to some 25 high-energy odd levels ( $60791.5$  to  $73244.8$  cm<sup>-1</sup>). It is seen that the latter set of odd levels is completely interlaced and surrounded by the even levels with which they combine. Consequently, only fringe combinations of these odd and even levels have been observed, and a considerable number of permitted combinations must exist in the unexplored infrared.

The inner quantum number ( $J$ -value) assigned to each level was originally based on the assumption that the first five odd levels have  $J$ -values  $1\frac{1}{2}$ ,  $1\frac{1}{2}$ ,  $2\frac{1}{2}$ ,  $0\frac{1}{2}$ ,  $1\frac{1}{2}$ , respectively. These and the values for four even levels were verified in 1934 by

Zeeman patterns observed by Green and Barrows [8]. Because all As I levels of unlike parity are permitted to combine if their  $J$ -values differ by 0 or by  $\pm 1$ , the  $J$ -values of new levels are usually fixed unambiguously by the observed combinations, but there are still a few high levels whose  $J$ -values are uncertain by one unit.

After establishing a large number of atomic energy levels, mostly with definite  $J$ -values, the next ambition was to group and interpret these as spectral terms characteristic of various configurations of the valence electrons. Aside from eight levels identified by Zeeman effect, the remainder could be grouped and named only by applying interval and intensity rules and by comparison with analogous spectra of other elements, in particular with the Ni [19], P I [19], and Se II [20] spectra, which were not well known 20 years ago. This procedure consumed all the established As I levels except a few very high ones, which are retained as "miscellaneous levels" because they may represent fragments of terms approaching the ionization limit. At this stage it was possible to discard some false levels involving

doubly classified lines, and also to add some levels resting on a single combination, as for example those with  $J$ -value  $3\frac{1}{2}$ . For fixing the latter, strong lines, otherwise unclassified, were usually found in their expected places.

## 2. As I Multiplets

As a check on the consistency and plausibility of spectral term designations, the square arrays of consecutive level combinations were rewritten to display As I multiplets and electron configurations so that level separations and line intensities could be easily seen. These combinations, grouped into multiplets, are presented in table 2 (ultraviolet) and table 3 (infrared and visible). All of the observed combinations are included in these tables except three that account for five lines due to transitions from  $5p\ ^4D^\circ$  to higher levels. From tables 2 and 3 stem the "Term combination" entered in column 5 of table 1 for each classified As I line, and also the difference between observed and calculated wave number shown in column 4 of table 1.

TABLE 2. As I combination of odd and even terms

Desig.	Desig. Level	$4p^3\ ^4S^{\frac{1}{2}}_{\frac{1}{2}}$ 0.0	$4p^3\ ^2D^{\frac{3}{2}}_{\frac{3}{2}}$ 10914.6	$4p^3\ ^2D^{\frac{5}{2}}_{\frac{5}{2}}$ 10592.5	$4p^3\ ^2P^{\frac{1}{2}}_{\frac{1}{2}}$ 18647.5	$4p^3\ ^2P^{\frac{3}{2}}_{\frac{3}{2}}$ 18186.1
$4p^4\ ^4P^{\frac{3}{2}}_{\frac{3}{2}}$ $4p^4\ ^4P^{\frac{1}{2}}_{\frac{1}{2}}$ $4p^4\ ^4P^{\frac{5}{2}}_{\frac{5}{2}}$	55366.4 56863.6 57488.1	55366.4 (200) 56863.6 (100) *57488.1 (60)				
$4p^4\ ^2D^{\frac{3}{2}}_{\frac{3}{2}}$ $4p^4\ ^2D^{\frac{5}{2}}_{\frac{5}{2}}$	68402.7 68300.6	68403.0 (3eg?) 68301.1 (2e)	*57488.1 (60) 57385.8 (10)	57810.2 (30) 57708.1 (30)	49755.1 (100r) 49653.1 (100)	50114.5 (100r)
$4p^4\ ^2P^{\frac{1}{2}}_{\frac{1}{2}}$ $4p^4\ ^2P^{\frac{3}{2}}_{\frac{3}{2}}$	61811.5 65497.4	64811.3 (4) 65497.3 (2)	53897.0 (10)	54219.3 (40) 54905.2 (2)	46163.8 (150) 46849.9 (50)	46625.3 (100) 47311.3 (100)
$4p^4\ ^2S^{\frac{1}{2}}_{\frac{1}{2}}$	66588.3			55996.1 (3)	47940.6 (30)	48402.2 (50)
$5s\ ^4P^{\frac{3}{2}}_{\frac{3}{2}}$ $5s\ ^4P^{\frac{1}{2}}_{\frac{1}{2}}$ $5s\ ^4P^{\frac{5}{2}}_{\frac{5}{2}}$	52897.9 51610.2 50693.8	52898.2 (2000R) 51610.4 (1500R) 50694.0 (1000R)	41983.2 (150r) 40695.5 (200r)	42305.2 (10) 41017.7 (50) 40101.7 (50)	34250.4 (2) 32962.7 (40) 32046.1 (50)	33424.0 (20) 32507.5 (20)
$5s\ ^2P^{\frac{1}{2}}_{\frac{1}{2}}$ $5s\ ^2P^{\frac{3}{2}}_{\frac{3}{2}}$	54605.3 53135.6	54606.0 (50) 53136.1 (40)	43690.5 (500R)	44012.8 (50) 42543.0 (500R)	35957.8 (200r) 34488.0 (50r)	36419.1 (50r) 34949.4 (100r)
$5s'\ ^2D^{\frac{3}{2}}_{\frac{3}{2}}$ $5s'\ ^2D^{\frac{5}{2}}_{\frac{5}{2}}$	60815.0 60834.8	60815.0 (5) 60835.0 (2)	49900.4 (300r) 49920.3 (20)	50222.7 (100r) 50242.4 (200r)	42167.5 (100r) 42187.1 (80r)	42648.5 (50)
$5s''\ ^2S^{\frac{1}{2}}_{\frac{1}{2}}$	72399.4				53751.9 (80)	54213.2 (40)
$6s\ ^4P^{\frac{3}{2}}_{\frac{3}{2}}$ $6s\ ^4P^{\frac{1}{2}}_{\frac{1}{2}}$ $6s\ ^4P^{\frac{5}{2}}_{\frac{5}{2}}$	69314.8 67920.2 67008.7	69315.0 (5) 67920.0 (4) 67008.9 (4)	58400.3 (10) 57005.7 (10)	58722.0 (3) 56416.2 (8)	50667.5 (3) 49272.8 (2) 48361.2 (20)	49734.0 (20) 48822.6 (50)
$6s\ ^2P^{\frac{1}{2}}_{\frac{1}{2}}$ $6s\ ^2P^{\frac{3}{2}}_{\frac{3}{2}}$	69696.2 68314.5		58781.3 (30)	57722.1 (30)	51048.8 (40r) 49666.9 (15)	51510.3 (5) 50128.3 (20)
$4d\ ^4P^{\frac{3}{2}}_{\frac{3}{2}}$ $4d\ ^4P^{\frac{1}{2}}_{\frac{1}{2}}$ $4d\ ^4P^{\frac{5}{2}}_{\frac{5}{2}}$	62751.1 63503.6 63981.7	62751.0 (100R) 63503.4 (30r) 63981.6 (10)	51836.6 (3) 52589.0 (5)	52159.1 (20) 52911.4 (5) 53389.6 (40)	44103.3 (25) 44856.0 (20) 45334.0 (10)	45317.4 (15) 45795.5 (20)
$4d\ ^2F^{\frac{3}{2}}_{\frac{3}{2}}$ $4d\ ^2F^{\frac{5}{2}}_{\frac{5}{2}}$	66785.2 64639.5		55870.6 (50)	54047.0 (40)		
$4d\ ^2D^{\frac{3}{2}}_{\frac{3}{2}}$ $4d\ ^2D^{\frac{5}{2}}_{\frac{5}{2}}$	66725.4 64342.4	64342.2 (4)	55810.7 (40) 53427.9 (30)	56133.1 (50) 53750.1 (80)	48077.7 (7) 45694.7 (5)	
$4d\ ^2P^{\frac{1}{2}}_{\frac{1}{2}}$ $4d\ ^2P^{\frac{3}{2}}_{\frac{3}{2}}$	66485.2 64122.0	66485.4 (2) 64121.9 (4)	55570.7 (2)	55892.8 (15)	47837.6 (6) 45474.6 (5)	48298.8 (30) 45935.9 (5)
$4d'\ ^2P^{\frac{1}{2}}_{\frac{1}{2}}$ $4d'\ ^2P^{\frac{3}{2}}_{\frac{3}{2}}$	72125.0 71924.4		61210.4 (5)	61532.0 (1) 61331.6 (4)	53477.6 (15) 53277.1 (2)	53938.9 (3) 53738.3 (5)
$4d''\ ^2D^{\frac{3}{2}}_{\frac{3}{2}}$ $4d''\ ^2D^{\frac{5}{2}}_{\frac{5}{2}}$	74453.1 74810.5		63538.5 (60) 63895.7 (7)	64217.8 (30)	56163.4 (50)	

TABLE 2. As I combination of odd and even terms—Continued

Desig.	Desig. Level	$4p^3\ ^4S_{1\frac{1}{2}}$ 0.0	$4p^3\ ^2D_{\frac{3}{2}}$ 10914.6	$4p^3\ ^2D_{\frac{5}{2}}$ 10592.5	$4p^3\ ^2P_{\frac{1}{2}}$ 18647.5	$4p^3\ ^2P_{\frac{3}{2}}$ 18186.1
	69644.8 69698.3 71055.2 72519.4 72779.0	69697.6 (3e)	58783.4 (15) 60141.0 (2) 61604.4 (2) 61864.5 (6)	59106.2 (7) 60462.4 (4) 61926.5 (5) 62186.3 (3)	50997.2 (2) 51051.1 (20) 52407.3 (1) 53872.3 (2) 54132.5 (10)	51458.9 (2e) 52868.9 (5) 54333.6 (10) 54592.9 (30)
	73566.0 73635.0 74049.7 74143.8 75086.0		62651.5 (2) 62719.9 (1e) 63135.3 (2)	62973.5 (20) 63457.0 (20)	54987.7 (5h) 55496.4 (3) 56438.5 (2)	55449.0 (10h) 55957.5 (6) 56900.0 (4)
	75176.4 75578.7 75799.4 76076.2 76835.6		64261.6 (40) 64664.2 (2) 65161.4 (4) 65920.9 (1e)	64986.1 (20) 65206.0 (3) 66242.7 (3)	†56530.1? (5) 56931.1 (2h) 57152.0 (1eh) 57429.0 (10) 58188.6 (1)	57613.6 (3) 57891.1 (4)?
	77121.7 77272.5		66207.2 (6h) 66357.4 (2)		58474.1 (7h) 58625.6 (4)	

\*Blend.

†Blend with As II?

TABLE 3. As I Combinations of even and odd terms

Desig	Desig Level	$5s\ ^4P_{\frac{3}{2}}$ 52897.9	$5s\ ^4P_{\frac{1}{2}}$ 51610.2	$5s\ ^4P_{\frac{5}{2}}$ 50693.8	$5s\ ^2P_{\frac{1}{2}}$ 54605.3	$5s\ ^2P_{\frac{3}{2}}$ 53135.6	$5s'\ ^2D_{\frac{3}{2}}$ 60815.0	$5s'\ ^2D_{\frac{1}{2}}$ 60834.8
$5p\ ^4D_{\frac{3}{2}}$ $5p\ ^4D_{\frac{5}{2}}$ $5p\ ^4D_{\frac{1}{2}}$ $5p\ ^4D_{\frac{5}{2}}$	62871.2 61685.0 60860.0 60791.5	9973.30 (400) 8787.19 (4)	10074.78 (400) 9249.78 (50) 9181.22 (20)	10166.26 (300) 10097.68 (150)				
$5p\ ^4P_{\frac{3}{2}}$ $5p\ ^4P_{\frac{1}{2}}$ $5p\ ^4P_{\frac{5}{2}}$	63282.8 62398.0 62026.3	10384.93 (400)	11672.62 (100) 10787.70 (150) 10416.04 (300)	11704.20 (50) 11332.41 (150)	8677.54 (10)	9262.42 (8) 8890.79 (10)		
$5p\ ^4S_{\frac{1}{2}}$	63647.0	10749.04 (250)	12036.75 (50)			10511.4 (3)		
$5p\ ^2D_{\frac{3}{2}}$ $5p\ ^2D_{\frac{1}{2}}$	64169.2 62554.4	11271.30 (100)	12558.94 (30) 10944.17 (50)	11860.66 (100)	9563.93 (100)	9418.87 (200)		
$5p\ ^2P_{\frac{1}{2}}$ $5p\ ^2P_{\frac{3}{2}}$	64687.6 64323.8		12713.61 (4)		10082.24 (200) 9718.49 (50)	11551.99 (100) 11188.17 (50)		
$5p\ ^2S_{\frac{1}{2}}$	64059.0				9453.65 (100)			
$5p'\ ^2F_{\frac{3}{2}}$ $5p'\ ^2F_{\frac{5}{2}}$	70927.5 70821.4		19211.24 (4)				10112.49 (100) 10006.40 (5)	9986.65 (100)
$5p'\ ^2D_{\frac{3}{2}}$ $5p'\ ^2D_{\frac{1}{2}}$	70376.6 70108.4				15771.16 (40)		9561.60 (20)	9541.83 (4) 9273.59 (5)
$5p'\ ^2P_{\frac{1}{2}}$ $5p'\ ^2P_{\frac{3}{2}}$	71193.7 71796.2		20321.65 (2) 20185.96 (10)		17190.97 (2h)	18796.16 (5) 18660.53 (1h?)	11116.65 (20)	11097.02 (2) 10961.52 (10)
$6p\ ^4D_{\frac{3}{2}}$ $6p\ ^4D_{\frac{5}{2}}$ $6p\ ^4D_{\frac{1}{2}}$ $6p\ ^4D_{\frac{5}{2}}$	72341.6 71131.0 70516.6 70274.9	19443.68 (100)	19520.72 (100)	19822.74 (50) 19581.09 (30) Cu?	16525.78 (5h)	17380.90 (5h)	10316.20 (10) 9701.54 (5)	9681.88 (10)
$6p\ ^4P_{\frac{3}{2}}$ $6p\ ^4P_{\frac{1}{2}}$ $6p\ ^4P_{\frac{5}{2}}$	72501.9 70849.7 69881.5	19603.97 (60)	20891.64 (3k) 19239.49 (50)	19187.68 (20)				
$6p\ ^4S_{\frac{1}{2}}$	72620.3	19722.35 (100)	21010.14 (5k)			19484.80 (80)		
$6p\ ^2D_{\frac{3}{2}}$ $6p\ ^2D_{\frac{1}{2}}$	72944.4 71621.4	20046.48 (6h)	20011.13 (8)	20927.72 (1h)	18339.10 (150)	18485.56 (100)	12129.43 (20)	(10786.6) §
$6p\ ^2P_{\frac{1}{2}}$ $6p\ ^2P_{\frac{3}{2}}$	73244.8 72800.6				18639.23 (60) 18195.31 (5)	19665.02 (10)	12429.83 (8)	12410.13 (5h) 11965.82 (10)
$6p\ ^2S_{\frac{1}{2}}$	71199.1		19588.84 (20)			18063.57 (3)		10364.4 (3)

§ Calculated wave numbers line masked.



TABLE 4.—As I predicted and observed terms

Electron configuration	Limit As II	Predicted	Observed
$4s^2 4p^3$		$4S^\circ \ ^2(P^\circ D^\circ)$	$4p^3 \ ^4S^\circ, 4p^3 \ ^2P^\circ, 4p^3 \ ^2D^\circ$
$4s \ 4p^4$		$4P \ ^2(S P D)$	$4p^4 \ ^4P, 4p^4 \ ^2S, 4p^4 \ ^2P, 4p^4 \ ^2D$
$4p^5$		$2P^\circ$	
$4s^2 4p^2 ns$	$3P$ $1D$ $1S$	$4P \ ^2P$ $2D$ $2S$	$5s \ ^4P, 6s \ ^4P, 5s \ ^2P, 6s \ ^2P$ $5s' \ ^2D$ $5s'' \ ^2S$
$4s^2 4p^2 np$	$3P$ $1D$ $1S$	$4(S^\circ P^\circ D^\circ) \ ^2(S^\circ P^\circ D^\circ)$ $2(P^\circ D^\circ F^\circ)$ $2P^\circ$	$\{5p \ ^4S^\circ, 6p \ ^4S^\circ, 5p \ ^4P^\circ, 6p \ ^4P^\circ, 5p \ ^4D^\circ, 6p \ ^4D^\circ$ $5p \ ^2S^\circ, 6p \ ^2S^\circ, 5p \ ^2P^\circ, 6p \ ^2P^\circ, 5p \ ^2D^\circ, 6p \ ^2D^\circ$ $5p' \ ^2P^\circ, 5p' \ ^2D^\circ, 5p' \ ^2F^\circ$
$4s^2 4p^2 nd$	$3P$ $1D$ $1S$	$4(P D F) \ ^2(P D F)$ $2(S P D F G)$ $2D$	$4d \ ^4P, 4d \ ^2P, 4d \ ^2D, 4d \ ^2F$ $4d' \ ^2P$ $4d'' \ ^2D$

### 3. As I Spectral Terms

Arsenic has atomic number 33, and the neutral atoms have electronic structure as follows:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ . The first spectrum of arsenic arises from changes in atomic energy resulting from alterations of the principal quantum numbers and total momenta of the last-named five valence electrons. The theoretical spectral terms associated with various configurations of electrons [21] are listed in table 4.

It was stated above that the empirically established atomic energy levels derived from analysis of the As I spectrum occur in three groups (1) five odd levels of low energy content (including zero, the normal state), (2) about 50 even levels of higher energy, and (3) some 25 odd levels intermingled with group (2). That group 1 is identified with the normal configuration  $4s^2 4p^3$  is verified by many experimental facts including line intensities, self-reversals, and Zeeman patterns. Group 2 arises in part from the configuration  $4s \ 4p^4$ , which yields eight levels,  $4P_{2\frac{1}{2}}, 4P_{1\frac{1}{2}}, 4P_{0\frac{1}{2}}, 2S_{0\frac{1}{2}}, 2P_{0\frac{1}{2}}, 2P_{1\frac{1}{2}}, 2D_{1\frac{1}{2}}, 2D_{2\frac{1}{2}}$ , all of which have been selected with the aid of analogous spectra as guides. The remainder of group 2 must be ascribed to  $4s^2 4p^2 ns$  and  $4s^2 4p^2 nd$ , whereas group 3 can originate only in  $4s^2 4p^2 np$ . There is, naturally, no difficulty about distinguishing even and odd levels, but the proper choice of even levels for terms due to  $ns$  and  $nd$  electrons added to  $4s^2 4p^2$  is complicated by overlapping of energies of the different electron configurations. These configurations give rise respectively to 8 and 28 levels, which converge toward five limits ( $3P_0, 3P_1, 3P_2, 1D_2, 1S_0$ ) in the As II spectrum when the running electron is removed by ionization. According to Rao [13], these levels in the As II spectrum have the following values in  $\text{cm}^{-1}$ :  $3P_0=0$ ;  $3P_1=1063$ ,  $3P_2=2540$ ,  $1D_2=10095$ ,  $1S_0=22599$ . Guided by these intervals in

convergence limits, we have provisionally interpreted the observed As I even levels as shown in table 4. Although the configuration  $4s^2 4p^3$  yields only five levels, including the ground term of As I, if the total quantum number is altered for one of the  $p$  electrons so that they are not all equivalent, the configuration produces no less than 21 levels, which converge also to the above mentioned five limits in As II. Terms associated with  $5p$  and  $6p$  electrons have been identified, as indicated in table 4. Ten hazy lines from 4910.23 to 4301.56 Å could not be classified; they may represent some leading combinations of terms arising from  $7p$  electrons with those from  $5s$ .

Full particulars (except  $g$  values) regarding the now known terms of the As I spectrum are presented in table 5, where columns 1 to 5 contain (1) electron configuration (and convergence limit), (2) term designation, (3) level value (relative to  $4p^3 \ ^4S_{1\frac{1}{2}}=0.0$ ), (4) intervals between levels of terms, and (5) combinations observed for each term.

### 4. First Ionization Potential of Arsenic

In 1942, before the ultraviolet portion of the As I spectrum had been satisfactorily observed, an attempt was made to obtain a value of the effective quantum number of the  $5s$  electron for As by comparing the values of neighboring elements and thus arrive at an estimate of the ionization potential. The result was not published, but it will be given here because it adds credence to the value recently derived from spectral series. The effective quantum numbers,  $n^*=\sqrt{R/T}$ , corresponding to  $5s$  in spectra of elements flanking As are shown in table 6.

By interpolation, the  $5s$  value of  $n^*$  for As I is found to be about 1.960. The corresponding term,  $T=R/n^{*2}$ , has a numerical value of  $109737/(1.960)^2=28565$ , and if this is added to the wave number 50694 of the resonance line (1972.62 Å), a value of 79259

TABLE 5. *Terms of the As I spectrum*

Electron configuration	Term designation	Level $\text{cm}^{-1}$	Interval $\text{cm}^{-1}$	Combinations
1	2	3	4	5
$4s^2 4p^3$	$4p^3 {}^4S_{1/2}$	0.0		$\{4p^3 {}^4P, 5s {}^4P, 6s {}^4P, 4d {}^4P, 4p^4 {}^2P, 5s {}^2P, 4d {}^2P, 4p^4 {}^2D, 5s' {}^2D, 4d {}^2D, 69698.$
$4s^2 4p^3$	$4p^3 {}^2D_{1/2}$ $4p^3 {}^2D_{3/2}$	10592.5 10914.6	322.1	$\{5s {}^4P, 6s {}^4P, 4d {}^4P, 4p^4 {}^2S, 4p^4 {}^2P, 5s {}^2P, 6s {}^2P, 4d {}^2P, 4d' {}^2P, 4p^4 {}^2D, 5s' {}^2D, 4d {}^2D, 4d' {}^2D, 4d {}^2F, 69698, 71055, 72519, 72779, 73566, 73635, 74049, 75176, 75578, 75799, 76076, 76835, 77121, 77272.$
$4s^2 4p^3$	$4p^3 {}^2P_{0/2}$ $4p^3 {}^2P_{1/2}$	18186.1 18647.5	461.4	$\{5s {}^4P, 6s {}^4P, 4d {}^4P, 4p^4 {}^2S, 5s' {}^2S, 4p^4 {}^2P, 5s {}^2P, 6s {}^2P, 4d {}^2P, 4d' {}^2P, 4p^4 {}^2D, 5s' {}^2D, 4d {}^2D, 4d' {}^2D, 69644, 69698, 71055, 72519, 72779, 73635, 74143, 75086, 75176, 75578, 75799, 76076, 76835, 77121, 77272.$
$4s^2 4p^2({}^3P)5s$	$5s {}^4P_{0/2}$ $5s {}^4P_{1/2}$ $5s {}^4P_{2/2}$	50693.8 51610.2 52897.9	916.4 1287.7	$\{4p^3 {}^4S^{\circ}, 5p {}^4S^{\circ}, 6p {}^4S^{\circ}, 5p {}^4P^{\circ}, 6p {}^4P^{\circ}, 5p {}^4D^{\circ}, 6p {}^4D^{\circ}, 6p {}^2S^{\circ}, 4p^3 {}^2P^{\circ}, 5p {}^2P^{\circ}, 5p' {}^2P^{\circ}, 4p^3 {}^2D^{\circ}, 5p {}^2D^{\circ}, 6p {}^2D^{\circ}, 5p' {}^2F^{\circ}.$
$4s^2 4p^2({}^3P)5s$	$5s {}^2P_{0/2}$ $5s {}^2P_{1/2}$	53135.6 54605.3	1469.7	$\{4p^3 {}^4S^{\circ}, 5p {}^4S^{\circ}, 6p {}^4S^{\circ}, 5p {}^4P^{\circ}, 6p {}^4D^{\circ}, 5p {}^2S^{\circ}, 6p {}^2S^{\circ}, 4p^3 {}^2P^{\circ}, 5p {}^2P^{\circ}, 6p {}^2P^{\circ}, 5p' {}^2P^{\circ}, 4p^3 {}^2D^{\circ}, 5p {}^2D^{\circ}, 6p {}^2D^{\circ}, 5p' {}^2D^{\circ}.$
$4s 4p^4$	$4p^4 {}^4P_{2/2}$ $4p^4 {}^4P_{1/2}$ $4p^4 {}^4P_{0/2}$	55366.4 56863.6 57488.1	-1497.2 -624.5	$\}4p^3 {}^4S^{\circ}.$
$4s^2 4p^2({}^3P)5p$	$5p {}^4D_{0/2}$ $5p {}^4D_{1/2}$ $5p {}^4D_{3/2}$ $5p {}^4D_{5/2}$	60791.5 60860.0 61685.0 62871.2	68.5 825.0 1186.2	$\}5s {}^4P, 4d' {}^2P, 4d'' {}^2D, 75176.$
$4s^2 4p^2({}^1S)5s$	$5s' {}^2D_{2/2}$ $5s' {}^2D_{1/2}$	60815.0 60834.8	-19.8	$\{4p^3 {}^4S^{\circ}, 6p {}^4D^{\circ}, 6p {}^2S^{\circ}, 4p^3 {}^2P^{\circ}, 6p {}^2P^{\circ}, 5p' {}^2P^{\circ}, 4p^3 {}^2D^{\circ}, 6p {}^2D^{\circ}, 5p' {}^2D^{\circ}, 5p' {}^2F^{\circ}.$
$4s^2 4p^2({}^3P)5p$	$5p {}^4P_{0/2}$ $5p {}^4P_{1/2}$ $5p {}^4P_{2/2}$	62026.3 62398.0 63282.8	371.7 884.8	$\}5s {}^4P, 5s {}^2P.$
$4s^2 4p^2({}^3P)5p$	$5p {}^2D_{1/2}$ $5p {}^2D_{3/2}$	62554.4 64169.2	1614.8	$5s {}^4P, 5s {}^2P, 4d' {}^2P.$
$4s^2 4p^2({}^3P)4d$	$4d {}^4P_{2/2}$ $4d {}^4P_{1/2}$ $4d {}^4P_{0/2}$	62751.1 63503.6 63981.7	-752.5 -478.1	$\}4p^3 {}^4S^{\circ}, 4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s^2 4p^2({}^3P)5p$	$5p {}^4S_{1/2}$	63647.0		$5s {}^4P, 5s {}^2P.$
$4s^2 4p^2({}^3P)5p$	$5p {}^2S_{0/2}$	64059.0		$5s {}^2P.$
$4s^2 4p^2({}^3P)4d$	$4d {}^2P_{0/2}$ $4d {}^2P_{1/2}$	64122.0 66485.2	2363.2	$4p^3 {}^4S^{\circ}, 4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s^2 4p^2({}^3P)5p$	$5p {}^2P_{0/2}$ $5p {}^2P_{1/2}$	64323.8 64687.6	363.8	$5s {}^4P, 5s {}^2P.$
$4s^2 4p^2({}^3P)4d$	$4d {}^2D_{1/2}$ $4d {}^2D_{2/2}$	64342.4 66725.4	2383.0	$4p^3 {}^4S^{\circ}, 4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s^2 4p^2({}^3P)4d$	$4d {}^2F_{2/2}$ $4d {}^2F_{3/2}$	64639.5 66785.2	2145.7	$4p^3 {}^2D^{\circ}.$
$4s 4p^4$	$4p^4 {}^2P_{1/2}$ $4p^4 {}^2P_{0/2}$	64811.5 65497.4	-685.9	$4p^3 {}^4S^{\circ}, 4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s 4p^4$	$4p^4 {}^2S_{0/2}$	66588.3		$4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s^2 4p^2({}^3P)6s$	$6s {}^4P_{0/2}$ $6s {}^4P_{1/2}$ $6s {}^4P_{2/2}$	67008.7 67920.2 69314.8	911.5 1394.6	$\}4p^3 {}^4S^{\circ}, 4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s 4p^4$	$4p^4 {}^2D_{1/2}$ $4p^4 {}^2D_{2/2}$	68300.6 68402.7	102.1	$4p^3 {}^4S^{\circ}, 4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s^2 4p^2({}^3P)6s$	$6s {}^2P_{0/2}$ $6s {}^2P_{1/2}$	68314.5 69696.2	1381.7	$4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
	$0\frac{1}{2}, 1\frac{1}{2}$	69644.8		$4p^3 {}^2P^{\circ}.$
	$1\frac{1}{2}, 2\frac{1}{2}$	69698.3		$4p^3 {}^4S^{\circ}, 4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s^2 4p^2({}^3P)6p$	$6p {}^4P_{0/2}$ $6p {}^4P_{1/2}$ $6p {}^4P_{2/2}$	69881.5 70849.7 72501.9	968.2 1652.2	$\}5s {}^4P.$
$4s^2 4p^2({}^1D)5p$	$5p' {}^2D_{1/2}$ $5p' {}^2D_{2/2}$	70108.4 70376.6	268.2	$5s {}^2P, 5s' {}^2D.$
$4s^2 4p^2({}^3P)6p$	$6p {}^4D_{0/2}$ $6p {}^4D_{1/2}$ $6p {}^4D_{2/2}$ $6p {}^4D_{3/2}$	70274.9 70516.6 71131.0 72341.6	241.7 614.4 1210.6	$\}5s {}^4P, 5s {}^2P, 5s' {}^2D.$
$4s^2 4p^2({}^1D)5p$	$5p' {}^2F_{2/2}$ $5p' {}^2F_{3/2}$	70821.4 70927.5	106.1	$5s {}^4P, 5s' {}^2D.$
	$1\frac{1}{2}$	71055.2		$4p^3 {}^2P^{\circ}, 4p^3 {}^2D^{\circ}.$
$4s^2 4p^2({}^3P)6p$	$6p {}^2S_{0/2}$	71199.1		$5s {}^4P, 5s {}^2P, 5s' {}^2D.$

TABLE 5. *Terms of the As I spectrum—Continued*

Electron configuration	Term designation	Level $\text{cm}^{-1}$	Interval $\text{cm}^{-1}$	Combinations
1	2	3	4	5
$4s^2 4p^2(^3P)6p$	$6p \ ^2D_{3/2}^{\circ}$	71621.4	1323.0	$5s \ ^4P, 5s \ ^2P, 5s' \ ^2D.$
	$6p \ ^2D_{5/2}^{\circ}$	72944.4		
$4s^2 4p^2(^1D)5p$	$5p' \ ^2P_{3/2}^{\circ}$	71796.2	135.5	$5s \ ^4P, 5s \ ^2P, 5s' \ ^2D.$
	$5p' \ ^2P_{1/2}^{\circ}$	71931.7		
$4s^2 4p^2(^1D)4d$	$4d' \ ^2P_{3/2}^{\circ}$	71924.4	200.6	$5p \ ^4D^{\circ}, 4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}, 5p \ ^2D^{\circ}.$
	$4d' \ ^2P_{1/2}^{\circ}$	72125.0		
$4s^2 4p^2(^1S)5s$	$5s'' \ ^2S_{0/2}$	72399.4		$4p^3 \ ^2P^{\circ}.$
	$1\frac{1}{2}$	72519.4		
$4s^2 4p^2(^3P)6p$	$6p \ ^4S_{3/2}$	72620.3		$4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}.$
	$1\frac{1}{2}$	72779.0		
$4s^2 4p^2(^3P)6p$	$6p \ ^2P_{3/2}$	72800.6	444.2	$5s \ ^2P, 5s' \ ^2D.$
	$6p \ ^2P_{1/2}$	73244.8		
	$1\frac{1}{2}, 2\frac{1}{2}$	73566.0		$4p^3 \ ^2D^{\circ}.$
	$1\frac{1}{2}$	73635.0		
	$1\frac{1}{2}, 2\frac{1}{2}$	74049.7		$4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}.$
	$0\frac{1}{2}, 1\frac{1}{2}$	74143.8		
$4s^2 4p^2(^1S)4d$	$4d'' \ ^2D_{3/2}$	74453.1	-357.4	$5p \ ^4D^{\circ}, 4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}.$
	$4d'' \ ^2D_{1/2}$	74810.5		
	$0\frac{1}{2}, 1\frac{1}{2}$	75086.0		$4p^3 \ ^2P^{\circ}.$
	$1\frac{1}{2}, 2\frac{1}{2}$	75176.4		
	$1\frac{1}{2}, 2\frac{1}{2}$	75578.7		$5p \ ^4D^{\circ}, 4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}.$
	$0\frac{1}{2}, 1\frac{1}{2}$	75799.4		
	$1\frac{1}{2}$	76076.2		$4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}.$
	$1\frac{1}{2}, 2\frac{1}{2}$	76835.6		
	$1\frac{1}{2}, 2\frac{1}{2}$	77121.7		$4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}.$
	$1\frac{1}{2}, 2\frac{1}{2}$	77272.5		
As II ( $^3P_0$ )	Limit	79165		$4p^3 \ ^2P^{\circ}, 4p^3 \ ^2D^{\circ}.$

$\text{cm}^{-1}$  is obtained for the limit ( $^3P_0$  of As II). This corresponds to a value of  $79259 \times 1.2395 \times 10^{-4} = 9.82$  ev for the principal ionization potential of arsenic.

In January 1950, after our ultraviolet As lines had been assembled and classified, it was observed that three high even levels (67009, 67920, 69315  $\text{cm}^{-1}$ ) had the same  $J$ -values and nearly the same separations as the three lowest even levels (50694, 51610, 52898  $\text{cm}^{-1}$ ). Since the latter group had already been identified as  $5s \ ^4P_{0\frac{1}{2}}, 1\frac{1}{2}, 2\frac{1}{2}$ , it was natural to regard the higher group as  $6s \ ^4P_{0\frac{1}{2}}, 1\frac{1}{2}, 2\frac{1}{2}$ . While writing this paragraph, we observed that Rao [12] interpreted these levels in exactly this way but

nevertheless arrived at an erroneous value of the ionization potential. Because the line intensities corresponding to transitions from these terms to the ground state are in the ratio of several hundred to one, it seems hopeless to detect similar levels of  $7s$ , and we must be content with two terms of a spectral series. With the aid of a Rydberg interpolation table, the effective quantum numbers and limits were calculated as shown in table 7.

The last column of table 7 contains three values of As I series limits corrected to the first level ( $^3P_0$ ) of As II. The average of these values is 79527  $\text{cm}^{-1}$ , which corresponds to 9.85 ev. Experience shows that the Rydberg formula generally yields too large

TABLE 6. *Effective quantum numbers  $n^*$  for  $5s$* 

Spectrum	Term	$T$	$R/T$	$n^* = \sqrt{R/T}$
29 Cu I	$5s \ ^2S_{0\frac{1}{2}}$	19180	5.724	2.3920
36 Zn I	$5s \ ^2S_{1/2}$	22094	4.967	2.229
31 Ga I	$5s \ ^2S_{0\frac{1}{2}}$	23592	4.651	2.157
32 Ge I	$5s \ ^3P_0$	26173	4.193	2.048
33 As I	$5s \ ^1P_{0\frac{1}{2}}$	28565	3.842	1.960
34 Se I	$5s \ ^1S_{1/2}$	36476	3.598	1.898
35 Br I	$5 \ ^4P_{2\frac{1}{2}}$	32120	3.416	1.848
36 Kr I	$5s \ ^3P_{1/2}$	32943	3.331	1.825
37 Rb I	$5s \ ^2S_{0\frac{1}{2}}$	33691	3.257	1.805

TABLE 7. *As I effective quantum numbers and series*

Electron	Lines $\text{cm}^{-1}$	Rydberg terms	$n^* = \sqrt{R/T}$	Limits in As II	Lowest limit
5s	50694	28948	1.947	$\} \ ^3P_0 = 79642$	79642
6s	67009	12633	2.947		
5s	51610	28941	1.947	$\} \ ^3P_1 = 80551$	79488
6s	67920	12631	2.947		
5s	52898	29094	1.942	$\} \ ^3P_2 = 81992$	79452
6s	69315	12677	2.942		



a limit, and a more reliable value will result from the use of a Ritz formula of the type,

$$\nu = L - R/(n + \mu + \alpha T)^2.$$

An examination of  $s$ -series represented by the Ritz formula in Zn I, Ga I, and Ge I spectra indicates that  $\alpha = 2.5 \times 10^{-6}$  for As I. On this assumption, the lowest limits in the final column of table 7 are calculated to be 79185, 79033, and 78995, respectively. The average of these values is  $79071 \text{ cm}^{-1}$ ; it corresponds to 9.80 eV and is in good agreement with 9.82 eV calculated with the interpolated effective quantum number for the  $5s$  electron. We believe that the average of these two figures,  $79165 \text{ cm}^{-1}$ , corresponding to  $9.81 \pm 0.01 \text{ eV}$ , gives a reliable value for the principal ionization potential of arsenic.

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